QUALITY CHARACTERIZATION AND PROCESS DESIGN OF SALMON OIL PRODUCTION FOR HUMAN CONSUMPTION

By

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QUALITY CHARACTERIZATION AND PROCESS DESIGN OF SALMON OIL PRODUCTION FOR HUMAN CONSUMPTION

A

THESIS

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Abstract

Salmon oil is an abundant source of polyunsaturated fatty acids, especially eicosapentaenoic acid and docosahexaenoic acid. Finding more lucrative markets for this unpurified fish oil requires well designed purification steps to reduce impurities such as free fatty acids (FFA), oxidative components, moisture, minerals, and trace metals. The temperature dependency of the rate constants for lipid oxidation and rheological properties of unpurified oil were measured and modeled using the Arrhenius equation. Performances of chitosan and/or activated earth as adsorbents were investigated to remove impurities from the oil. Activated earth was found more effective in adsorbing primary oxidation products than chitosan. Neither chitosan nor activated earth was effective in reducing FFA from the unpurified oil. Oils purified using activated earth adsorption, neutralization process, and/or combined neutralization and activated earth adsorption processes were characterized for peroxide value (PV), FFA, color, minerals, tocopherols, insoluble impurities, thermal properties, and viscosity. The neutralization process reduced FFA in the unpurified oil but PV increased. The combined method was more effective in reducing impurities than each individual process. The research findings from this study will provide a good model for purifying oil produced from salmon byproducts.

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General Introduction

The salmon fishing industry is one of the most important businesses in Alaska. Huge amounts of pink and red salmon are harvested in Alaska annually. In 2006, about 331,798 metric tons of salmon were harvested in Alaska (ADFG, 2007). Most wild salmon harvested in Alaska are either canned or headed and gutted (H&G). Processing yield for salmon varies depending on the final product form. The yield is 65-67% for canning and 72-75% for H&G. This means a potential supply of roughly 99,000 metric tons of salmon processing byproducts that could be used for making salmon oil. Sathivel (2005) reported that red salmon heads contained approximately 15-18% lipids.

Salmon oil is an abundant source of polyunsaturated fatty acids, especially eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA). Omega-3 fatty acids in fish oil are recognized for their great value to human health. The American Heart Association (AHA) reports that consumption of eicosapentaenoic and docosahexaenoic omega-3 fatty acid reduces the risk of coronary heart disease. According to the AHA, patients with coronary heart diseases should take fish oil daily (Harris, 2004). DHA and EPA are also reported to benefit the structure and function of brain system (Bourre et al., 1991). With the increasing demand of fish oil as healthy and functional food, the quality of fish oil producing is becoming extremely important to the industry.

Unpurified salmon oil contains various impurities including free fatty acids (FFA), phospholipids, minerals, crude proteins, moisture, and oxidation products. These impurities must be removed to produce good quality salmon oil for the nutraceutical market and to extend shelf life. Conventional fish oil purification steps

include degumming, neutralization, bleaching, and deodorizing. Phospholipids, protein and other compounds are removed by degumming and free fatty acids are precipitated as soaps and removed during the neutralization process. Oils are bleached by adsorption of pigments to clays and oxidized components are removed by deodorization (Brekke, 1980).

Adsorption and neutralization are two steps that can be used in purifying salmon oil. Adsorption is a cost effective process, which removes non-triglycerides materials in the unpurified oil (Proctor & Palaniappan, 1990; Sathivel, 2003a; Sathivel & Prinyawiwatkul, 2004). Adsorption is a process that involves the mass transfer of adsorbate from the fluid phase to the adsorbent surface until the thermodynamic equilibrium of the adsorbate concentration is reached. Therefore, adsorption kinetics is a fundamental property of adsorbate-adsorbent interaction. Theoretical and empirical models have been proposed to explain the adsorption process. Advantages of the adsorption technology compared to conventional refining methods are lower refining losses and less lipid oxidation in the refined oil. Adsorption technology can potentially provide a simplified process for refining salmon oil for human consumption. Neutralization is a process designed to neutralize free fatty acids in the oil using caustic soda. The process also precipitates some of the trace metals, and washes away phospholipids, pigments, proteins and other water soluble compounds from unpurified fish oil.

Selecting the most appropriate adsorbent to remove oxidation products, removing FFA of salmon oil and other impurities using neutralization processes, and predicting the performance of an adsorption system for salmon oil are worth investigation. The effects of neutralization and adsorption processes for salmon oil

have not been reported. The information in this study is valuable for salmon oil and will add value to oil produced from salmon byproducts and help the overall economy of the Alaska salmon industry.

There were two major objectives in this study. The first objective included (1) determining the thermal stability, melting point, specific heat capacity, enthalpy, and rheological properties and (2) determining the effects of temperature on the viscosity and oxidation rates of the salmon oil. The second objective included (1) evaluating the performance of activated earth or chitosan as an adsorbent to remove FFA and peroxides from the unpurified salmon oil, (2) purifying salmon oil using either the activated earth adsorption process, neutralization process, or combined neutralization and activated earth adsorption processes, (3) evaluating the adsorption kinetics using activated earth as an adsorbent to remove peroxides from both unpurified salmon oil and neutralized salmon oil, and (4) characterizing the unpurified salmon oil, activated earth adsorbed oil, neutralized oil, and neutralized and activate earth adsorbed oil.

Chapter 1

Thermal and rheological properties and the effects of temperature on the viscosity and oxidation rate of unpurified salmon oil[1]

Abstract

Thermal and rheological properties and oxidation rate of unpurified salmon oil were evaluated. The effects of temperature on the magnitude of viscosity and lipid oxidation rates of unpurified salmon oil were measured and modeled using the Arrhenius equation. The melting point of salmon oil ranged from – 61.3 to 31.2°C. The flow behavior index of the oil samples was less than one, which indicated that the salmon oil exhibited non-Newtonian fluid behavior. The apparent viscosity at 5°C was significantly higher ($P<0.05$) than those at 10, 15, 20, 25, 30, and 30, and 35°C. The average magnitude of activation energy for apparent viscosity of the oil was 21.8 kJ/mol. The predicted viscosity obtained by the Arrhenius equation agreed with the experimental viscosity. The rate of lipid oxidation for unpurified salmon oil was temperature dependent ($R^2 = 0.99$). The activation energy for lipid oxidation of the oil was 51.3 kJ/mol. This study demonstrated that the Arrhenius equation could be used to evaluate the lipid oxidation rate and to predict the apparent viscosity of unpurified salmon oil.

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[1]In preparation for submission to Food and Bioprocess Technology as: Huang J & Sathivel S. Thermal and rheological properties and the effects of temperature on the viscosity and oxidation rate of unpurified salmon oil.

Introduction

In year 2006, about 331,798 metric tons of salmon were harvested in Alaska (ADFG, 2007). On average, 94% of wild salmon harvested in Alaska are either canned or frozen headed and gutted. And over 99,000 metric tons of salmon byproducts are produced, which make up about 27% of the total weight of salmon harvested. Approximately 50,000 to 80,000 metric tons of salmon heads are produced as byproducts from the processing of both pink (*Oncorhynchus gorbuscha*) and red salmon (*Oncorhynchus nerka*) in Alaska. Much of the oil in salmon byproducts is found in the head, which contains approximately 15-18% lipid (Sathivel, 2005). Salmon oil is an excellent source of the omega-3, polyunsaturated fatty acids (n-3, PUFA), eicosapentaenoic acid (EPA), and docosahexaenoic acid (DHA). With the increasing demand of fish oil as healthy and functional food, the quality of the purified fish oil is extremely important and attention must be paid to remove impurities, such as free fatty acids, proteins, moisture, pigments, minerals, oxidation products, and volatile compounds from the oil.

Fish oil purification involves many unit operations. Knowledge of thermal, rheological, and oxidation properties of the salmon oil is essential for the design of purifying processes, the analysis of production cost, and the final quality evaluation. The thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) can be used to determine the quality of fish oil (Sathivel et al., 2003a; Sathivel, 2005). These methods require less time and provide precise data (Wesolowski & Erecinska, 1998). TG analysis is widely used to measure the thermal stability of various kinds of materials and is capable of depicting the mass changes of a sample material as a function of temperature during the thermal process (Gennaro et al., 1998). TG

analysis could be an alternative method of measuring salmon oil stability which requires smaller sample size and less time than the older techniques.

DSC offers a simple means to investigate the characteristics of salmon oil. The influence of composition of oil, content of water, production materials, aging and heat treatment on the oil quality can be demonstrated using DSC (Tan & Che Man, 2002). DSC analysis provides a precise and versatile approach to characterize physical properties such as melting point, enthalpy, and specific heat capacity of the fish oil (Sathivel, 2005). DSC has been used to investigate the thermal conductivity and specific heat (Buhri & Singh, 1994), melting and crystallization (Kaisersberger, 1989; Ritter et al., 2001), oil content (Iannotta et al., 2001), wax coating (Ritter et al, 2001), and phase transition (Lai and Chao, 2000) of foods.

Knowledge of the rheological properties of salmon oil helps to solve problems related to the transfer or movement of bulk quantities of the salmon oil. Nearly all procedures in fish oil purification use rheological property information. This information is essential in controlling the fluid transfer, velocity, and energy requirement for pumping and heating of fish oil. During purification, impurities such as FFA, proteins, moisture, pigments, minerals, oxidation products, and volatile compounds, are sequentially removed from the unpurified fish oil (Wiedermann, 1981). Removing impurities may alter the rheological properties of the fish oil (Sathivel et al., 2003b). Precise information on the rheological properties provides better control over fluid velocity, pump pressure, and energy consumption during the production of fish oil.

Marine fish oils, which contain high quantities of polyunsaturated fatty acids, are susceptible to oxidation. The lipid oxidation of the oil mostly depends on the

storage temperature and storage period (Aidos et al., 2002; Tan et al., 2001). Peroxide value (PV) provides information on the formation of primary oxidation products in the oil. A large amount of primary oxidation products present in the fish oil decreases the commercial value of fish oil, accelerates the lipid oxidation and decreases the product's shelf life (Aidos et al., 2002). The rate of the formation of primary oxidation products depends on temperatures and storage time (Frankel, 1998; Sathivel et al., 2007a; Aidos et al., 2002).

The temperature dependent viscosity and oxidation of salmon oil could be extrapolated by using the Arrhenius equation. The Arrhenius equation expresses the relationship between the rate constant and the activation energy of a reaction. A large number of reports are available on the mechanism of lipid oxidation and the influence of temperature on the quality of the oil. However, information on thermal stability, melting point, specific heat capacity, enthalpy, rheological properties, and lipid oxidation rates for salmon oil is not available. The information is essential for the design of a proper refining process, the analysis of production cost, and the final quality evaluation. Information on temperature influence on oxidation rate and changes in viscosity of salmon oil is needed to obtain reliable predictive models for assessing the quality of salmon oil.

The objectives of this study were to evaluate thermal stability, melting point, specific heat capacity, enthalpy, and rheological properties, and to determine the effects of temperature on the viscosity and oxidation rates of the salmon oil.

Materials and Methods

Salmon Oil Production

Unpurified salmon oil was produced from processing salmon byproducts including viscera, heads, skins, frame, and discarded fish obtained from a commercial seafood processing plant in Alaska as described in Figure 1.1. The byproducts were held at the fish processing plant at 8-14°C for 2-4 hours before being transported to the fish meal plant, where they were stored at 10-14°C for 4-48 hours before further processed into fish oil and fish meal. The byproducts were ground and cooked for about 20 min at 95°C. The cooked fish byproducts were then mechanically dewatered in a screw press, which subsequently produced press cake and press liquor. The press liquor was clarified using a decanter to remove suspended solids and then the clarified liquor was centrifuged to separate the oil and aqueous fraction. The resulting unpurified oil was collected from the fish meal plant and stored at -40°C until used at the University of Alaska Fairbanks, Fishery Industrial Technology Center, located in Kodiak, Alaska.

Color, Density, Specific Gravity and Water Activity

Color of salmon oil was measured in triplicate using a Minolta Chromameter (Model CR-300, Minolta Co., Ltd, Osaka, Japan). The data of colors were reported in CIELAB color scales (L*, a* and b* values). Chroma and hue angle value were calculated as $[a^{*2} + b^{*2}]^{1/2}$ and $\tan^{-1}$ (b*/a*), respectively. Bulk density of unpurified salmon oil was determined in triplicate using a 25 mL measuring cylinder at 20 ± 1°C. The sample was filled to a 25 mL cylinder, the weight to volume ratio determined, and

bulk density value reported as g per mL. Specific gravity was calculated in triplicate as the density of fish oil divided by the density of water at 20 ± 1°C. Water activity was measured using an AqualLab water activity meter (Model Series 3 TE, Decagon Devices, Inc., Pullman, WA) at 20 ± 1°C in triplicate.

Peroxide Value and Free Fatty Acids

The peroxide value (PV) of the unpurified salmon oil sample was measured by titration according to AOAC (1999). The results were expressed in terms of millimole of peroxides per kg of oil. Free fatty acids (FFA) content was determined using titrating according to AOCS (1998). The percentage of FFA was expressed as oleic acid equivalents.

Thermogravimetric Analysis (TGA)

A thermogravimetric analyzer (Model Q50; TA Instruments, Ltd, New Castle, DE) was used to determine the thermal stability of salmon oil. The thermogravimetric analyzer was calibrated with the curie standard for temperature accuracy and with a 100 mg standard for weight accuracy. Approximately 10 mg of the oil sample was added to a platinum pan. The pan was placed in the furnace and the exact sample weight was determined. The sample was programmed to be heated from 25°C to 700°C at the heating rate of 2°C/min. Sample weight differences were automatically recorded every 0.5 sec. The data were then plotted and analyzed with TA Universal Analyzer Software (Version 4.3A, TA Instruments, Ltd, New Castle, DE).

Differential Scanning Calorimetry (DSC) Analysis

A differential scanning calorimeter (DSC Model 2920; TA Instruments, Ltd, New Castle, DE) was used to determine the melting point, specific heat capacity, and enthalpy of the salmon oil sample. Approximately 1-5 mg of the unpurified salmon oil sample was placed in the aluminum sample vessel. The sample vessel was then placed on the sample platform while an empty aluminum vessel was placed on the reference platform. To determine the phase transition of the unpurified salmon oil, a linear heating rate of 5°C/min over a temperature range of -75 to 100°C was used. The data collected was plotted and the thermogram peak points were used to determine the melting points. A baseline was drawn through the beginning to the end of the endotherm peak. The area encircled by the peak and the baseline was integrated for estimating the enthalpy (ΔH). TA Universal Analyzer Software (Version 4.3A, TA Instruments, Ltd, New Castle, DE) was used to calculate the specific heat capacity from the DSC transition curve.

Rheological Properties of Salmon Oil

An Advanced Rheometer (Model AR2000; TA Instruments, Ltd, New Castle, DE) fitted with a cone plate geometry (acrylic plates with a 20-mm diameter, having a 200 µm gap between the two plates) was used to study the rheological properties of the oil samples at different temperatures. Approximately 0.1 gram of the oil sample was placed in the temperature-controlled parallel plate and allowed to equilibrate to 5, 10, 15, 20, 25, 30, or 35°C. The shear stress was measured at 5, 10, 15, 20, 25, 30, and 35°C at varying shear rates from 0 to $500s^{-1}$. The mean values of triplicate samples were reported.

The power law (Equation 1.1) was used to analyze the flow behavior index of the salmon oil sample at different temperatures.

$$\sigma = K\gamma^n \qquad (1.1)$$

where σ= shear stress (Pa.s), γ= shear rate (s^{-1}), K = consistency index ($Pa.s^n$), and n = flow behavior index. The natural logarithms were taken on both sides of Equation 1.1, and a plot of $ln\ \sigma$ versus $ln\ \gamma$ was constructed. The resulting straight line yielded the magnitude of $ln\ K$ (i.e., intercept) and n (i.e., slope).

The effect of temperature on apparent viscosity of the oil was expressed through the Arrhenius equation as described in Equation 1.2.

$$\mu = \mu_\infty \exp(E_a / RT) \qquad (1.2)$$

where μ_∞ is the frequency factor, *Ea* is the activation energy ($J.mol^{-1}$), R is the gas constant (8.314 $J.mol^{-1}.K^{-1}$), and T is the temperature (K). Apparent viscosity of the unpurified salmon oil sample was measured at 5, 10, 15, 20, 25, 30, and 35°C at a shear rate of 500 s^{-1} using the AR 2000 Rheometer. A plot of *ln* apparent viscosity versus *1/T* (i.e., 1/absolute temperature) was constructed for each salmon oil sample. The magnitude of *Ea* was calculated as the slope of the plot multiply by the gas constant, and μ_∞ was an exponential of the intercept. The viscosity values of the salmon oil were predicted using Equation 1.2 at 7, 12, 17, 22, 27, 32, and 37°C.

Oxidation Study of Salmon Oil

The PV of the unpurified salmon oil sample was measured according to AOAC (1999). The opened glass beaker containing the salmon oil was placed in a

water bath and heated at 30, 40, 50, 60, 70, 80 and/or 90°C. Samples were drawn every hour for the PV analysis for up to 8 hours. The oxidation rate was calculated as the amount of peroxides value increased every hour. The effect of temperature on the oxidation rate was described through the Arrhenius relationship as shown in Equation 1.3.

$$v = v_{\infty} \exp(-E_a / RT) \qquad (1.3)$$

where v is the oxidation rate; v_{∞} is frequency factor. The natural logarithms were taken on both sides of the equation and a linear relationship was developed between natural logarithm of the oxidation rate and inverse of the temperature. The slope and the intercept were calculated to yield v_{∞} (i.e., frequency factor) and *Ea* (i.e., activation energy). The oxidation rate of salmon oil was predicted at 35, 45, 55, 65, 75, and 85°C.

Statistical Analysis

Means and standard deviations of the data collected were reported. Analysis of Variance (ANOVA) and Tukey's studentized range test were performed to detect significant differences among the different treatments at the significant level of $P<0.05$ using SAS version 8.2 (SAS Institute Inc., 2002).

Results and Discussion

Color, Bulk Density, Specific Gravity and Water Activity

Information about color, bulk density, and water activity for salmon oil is given in Table 1.1. The unpurified salmon oil was dark red and yellow in color (L*

= 26.95; a* = 4.24; b* = 8.65). The color intensity (chroma) and the hue angle of the unpurified salmon oil were 9.64 and 28.07, respectively. The bulk density of the oil was 0.91 g/ml, which was similar to those values reported by Sathivel (2005) for red salmon oil (0.9 g/mL) and pink salmon oil (0.81 g/mL). The specific gravity was calculated as 0.92 for salmon oil at 20°C. The water activity of the oil (0.44) was lower than those values reported by Sathivel (2005) for red salmon oil (0.57) and pink salmon oil (0.53).

Thermogravimetric Analysis (TGA)

The TG curve (Figure 1.2) showed the thermal decomposition of the unpurified salmon oil. Initial decomposition began at 174°C, where the less thermal resistant substances in the oil sample first started to break down. Figure 1.3 showed a 0.6% weight increase in the unpurified oil between 92°C and 158°C, which might be attributed to lipid oxidation in the oil sample (Hassel, 1976). In an oxygen atmosphere, an onset of oxidation in the oil is characterized by oxygen absorption by the fatty acid, leading to a formation of oxidation products known as peroxides. This behavior is usually identified by an increase in the initial sample mass (Hassel, 1976). According to Van Aardt et al. (2004) and Milula & Khayat (1985), the TGA was a valuable technique for evaluating the oxidative stability difference between different oils and as well as evaluating the effects of different antioxidants.

Between 250°C to 550°C, the weight loss of the unpurified salmon oil drastically increased with increased heating temperature (Figure 1.2). The weight loss of the unpurified salmon oil taking place between 173 and 250 °C, 250and 350°C, 350 and 450°C, and 450 and 550°C was 6.2%, 45.5%, 31.5%, and 16.5%, respectively.

The unpurified salmon oil was not completely decomposed at 550°C as minerals, metals, and other high thermal resistant substances remained. Unpurified salmon oil contains phospholipids, metals, minerals, free fatty acids, and peroxides and their breakdown products, which are highly interactive with the oil (Wiedermann, 1981). Sathivel (2001) reported that the mineral content, free fatty acids and water activity of unrefined catfish oil decreased during refining process. The weight loss of edible oils due to thermal decomposition is higher in purified oils than unpurified oils. The higher value of the initial temperature of decomposition implies good quality of oil (Wesolowski & Erecinska, 1998). Sathivel et al. (2003a) reported that refining of catfish and menhaden oils tended to reduce their relative resistance to thermal decomposition.

Differential Scanning Calorimetry (DSC) Analysis

The DSC thermogram (Figure 1.4) shows three distinct endothermic peaks for the unpurified salmon oil. The melting point of the unpurified salmon oil ranged from -61.3 to 31.2°C, which was relatively wider than the reported melting point range of -69.6 to -0.36°C and -64.7 to 20.8°C for red and pink salmon oils, respectively (Sathivel, 2005). The low melting point of the salmon oil was attributed to triacylglycerol which contained unsaturated fatty acids (Tan & Chen Man, 2002). Oil samples with a higher degree of unsaturated fatty acids melt at lower temperatures, whereas those with a higher degree of saturated fatty acids melt at higher temperatures. The third peak appears around the temperature of -2.8 °C. This melting point at -2.8°C may be attributed to the presence of oleic acid (C18:1) and linoleic acid (C18:2), whose melting points range from -13.0 to 15.2°C. It also

might be attributed to moisture in the sample (Berjak et al., 1992; Conner & Bonner, 2001).

All three peaks for the unpurified salmon oil were not sharp; this might be attributed to the presence of impurities, such as phospholipids, ketones, and other materials in the unpurified fish oil (Sathivel, 2005). Sathivel et al. (2007b) reported that the DSC thermograms of purified fish oil showed sharper and narrower peaks than unpurified fish oil. The melting points of fish oil were sharper after each purification step that removed impurities from the oil.

The enthalpy of the salmon oil was 58.7 kJ/kg, which was higher than those (40 and 39 kJ/kg, respectively) reported for red and pink salmon oils (Sathivel, 2005) but was slightly lower than that (84.7 to 73.9 kJ/kg) reported for catfish oils (Sathivel et al., 2007b). The specific heat capacity for the unpurified salmon oil ranged from 0.26 to1.5 kJ/kg/^{o}C (Figure 1.4). The specific heat capacity of 0.8 to 1.6 kJ/kg/^{o}C was reported for red salmon oil while 1.3 to 2.3 kJ/kg/^{o}C for pink salmon oil (Sathivel, 2005). Enthalpy of the oil explains whether oil changes from one physical state to another either by absorbing (endothermic) or releasing (exothermic) heat (Zhao & Yalkowsky, 1999). Specific heat capacity is an important measure that provides information about the amount of energy that must be supplied or withdrawn to change temperature by a given amount. Information on thermal degradation, melting point, specific heat capacity, and enthalpy is useful for designing and optimizing unit operations for salmon oil purification.

Rheological Properties of Salmon Oil

The power law parameters for the unpurified salmon oil are given in Table 1.2. The flow behavior index (n) of the unpurified salmon oil sample ranged from 0.8 to 0.88, which indicated its slight non-Newtonian behavior. The consistency index (K) value for the unpurified salmon oil was higher at lower temperatures. Table 1.2 and Figure 1.5 indicate changes in apparent viscosity of the unpurified salmon oil as a function of temperature. The Arrhenius equation (Equation 1.2) was used to calculate the average magnitude of activation energy of the unpurified salmon oil from 1/T and the natural logarithm of the apparent viscosity (Figure 1.5). The activated energy (Ea) indicates the energy barrier that must be overcome before the elementary flow process can occur (Rao, 1999). The magnitudes of Ea (21.80 kJ/mol) and μ_∞ (5.7×10^{-6}) for the salmon oil are given in Table 1.2. The predicted viscosity obtained by the Arrhenius equation agreed with the experimental viscosity (Figure 1.6). The degree of fit, as shown by the R^2 value of 0.99 (Figure 1.6), indicated that changes in apparent viscosity with temperature could be modeled by the Arrhenius equation. This study showed that the magnitude of the apparent viscosity of the unpurified salmon oil was greatly influenced by temperature.

Oxidation Study of Salmon Oil

Figure 1.7 shows the changes in PV of the unpurified salmon oil as a function of time at different temperatures. PV is a useful indicator of lipid oxidation, especially at the beginning of the lipid oxidation (Choe & Min, 2005). The lipid oxidation, as indicated by the PV values, increased with increasing time and

temperature (Figure 1.7). The unpurified salmon oil stored at 30°C and 40°C for 8 hours exhibited minimal lipid oxidation, whereas those oils at 50-90°C showed higher lipid oxidation after 8 hours (Figure 1.7). The oxidation of oil sample at 90°C was similar to the oxidation rate at 80°C, which may be attributed to the decomposition of primary hydroperoxides occurring at higher temperature. Frankel (1998) and Aidos et al. (2002) reported that hydroperoxides degradation was higher at an elevated temperature; and therefore, may accumulate to an equal extent in the oil stored at 90°C and 80°C. The oxidation rates for the unpurified salmon oil were well fitted by the Arrhenius equation (Figure 1.8) and the R^2 value of 0.98 indicated that the peroxide formation rate could be modeled by the Arrhenius equation. The predicted lipid oxidation rates obtained by the Arrhenius equation agreed with the experimental values (Figure 1.9). The *Ea* value for lipid oxidation of the unpurified salmon oil was 51.3 kJ/mol, which was in accordance with the previously reported *Ea* values for lipid oxidation of edible oils (24 to 240 kJ/mol) (Frankel 1993; Tan et al., 2001). This study demonstrated that the rate of oxidation of the unpurified salmon oil was influenced by temperature.

Conclusion

This study provided information on thermal and rheological properties and lipid oxidation of unpurified salmon oil, which is useful for designing the purification process of the oil. It is important to be able to predict the apparent viscosity value of the oil at each purification step because each purification step of the salmon oil involves different temperature conditions. The salmon oil exhibited non-Newtonian

fluid behavior. The apparent viscosity of unpurified salmon oil was significantly higher at 5°C than those at 10, 15, 20, 25, 30, and 35°C. The lipid oxidation rate of the unpurified salmon oil was temperature dependent. The study showed that changes in the magnitude of apparent viscosity and the lipid oxidation rate of the unpurified salmon oil with temperature could be well described by the Arrhenius equation.

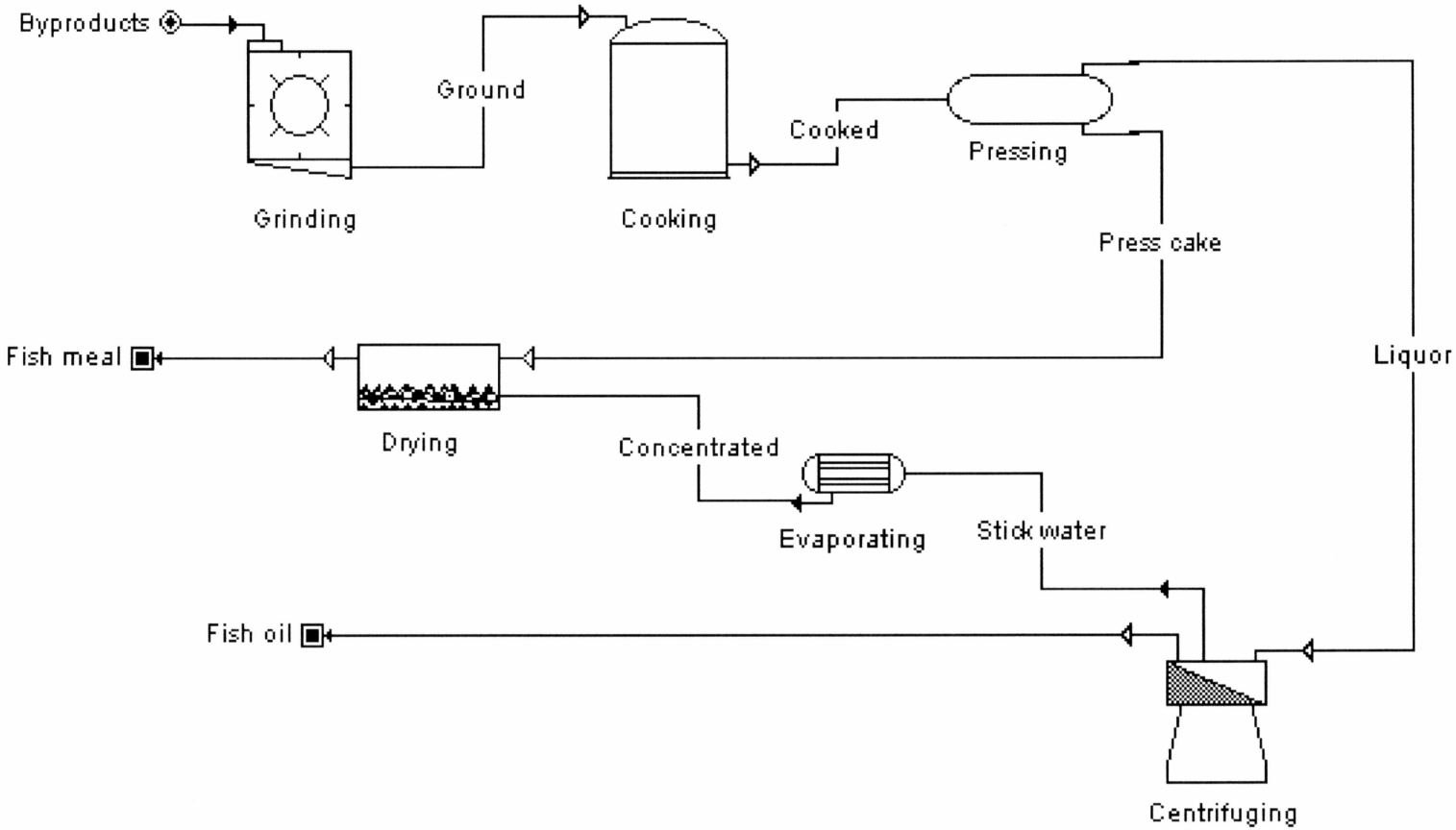

Figure 1.1 Production of unpurified salmon oil.

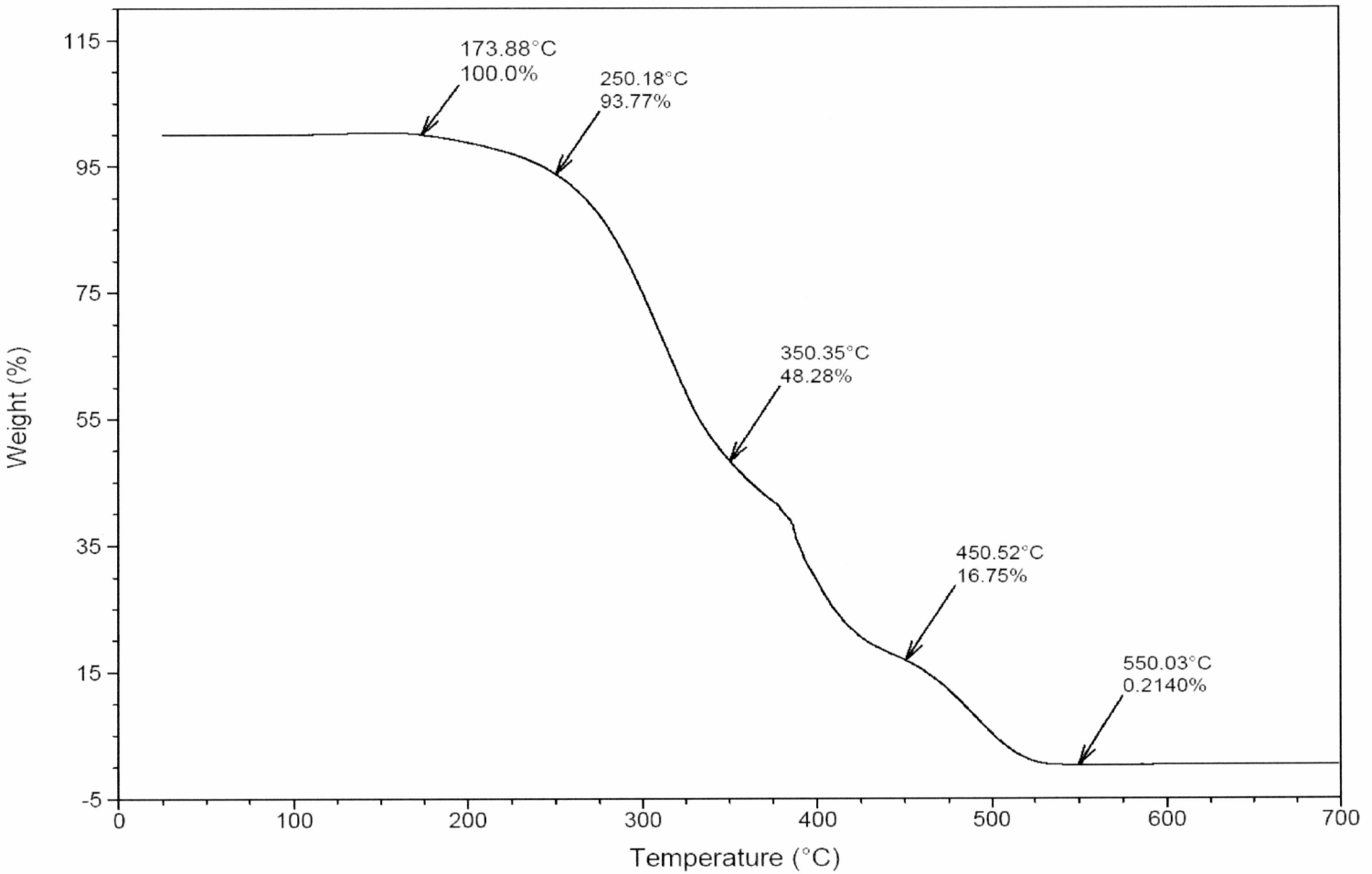

Figure 1.2 Representative TGA thermogram of unpurified salmon oil.

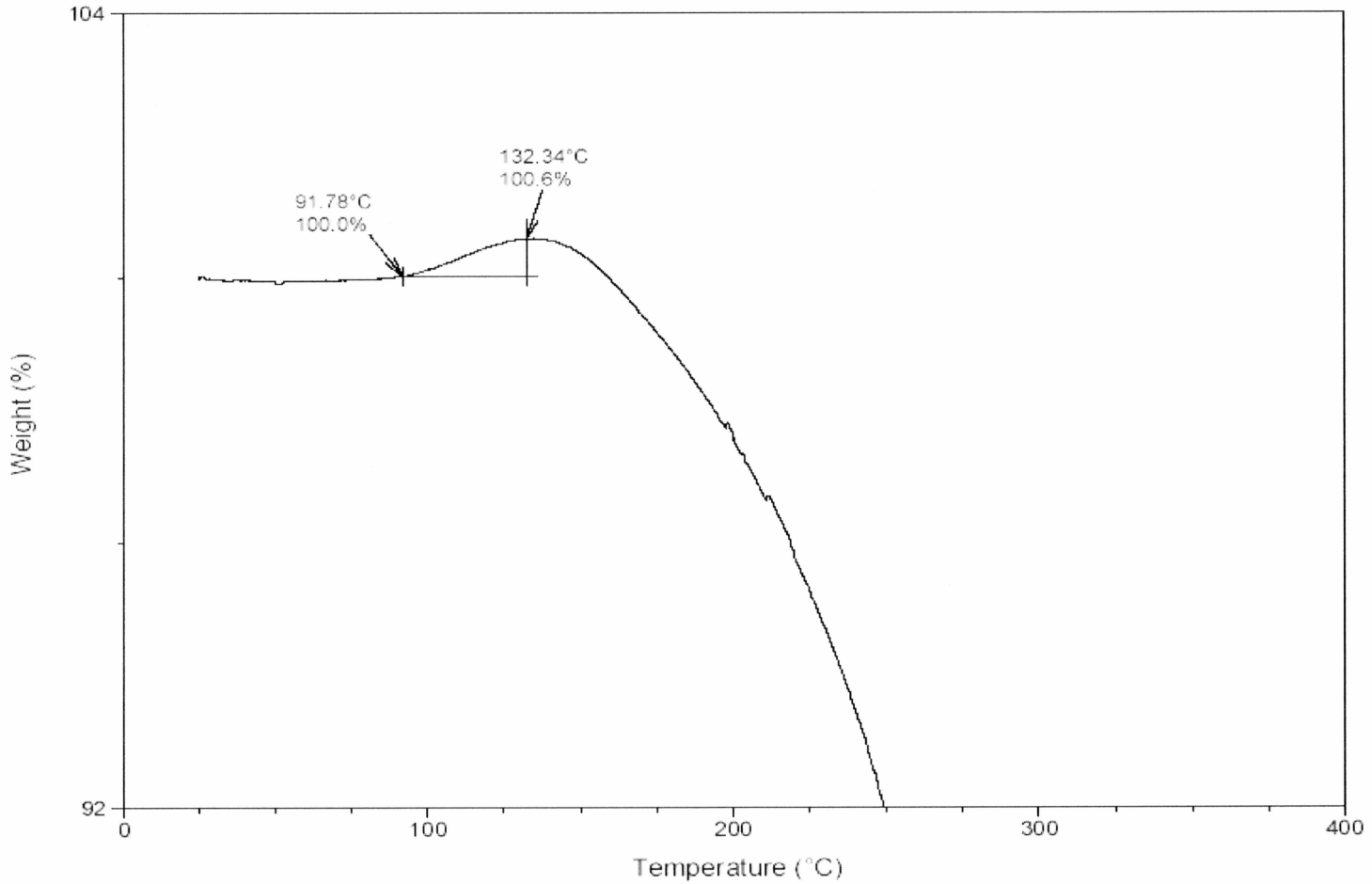

Figure 1.3 Representative TGA thermogram of unpurified salmon oil oxidation.

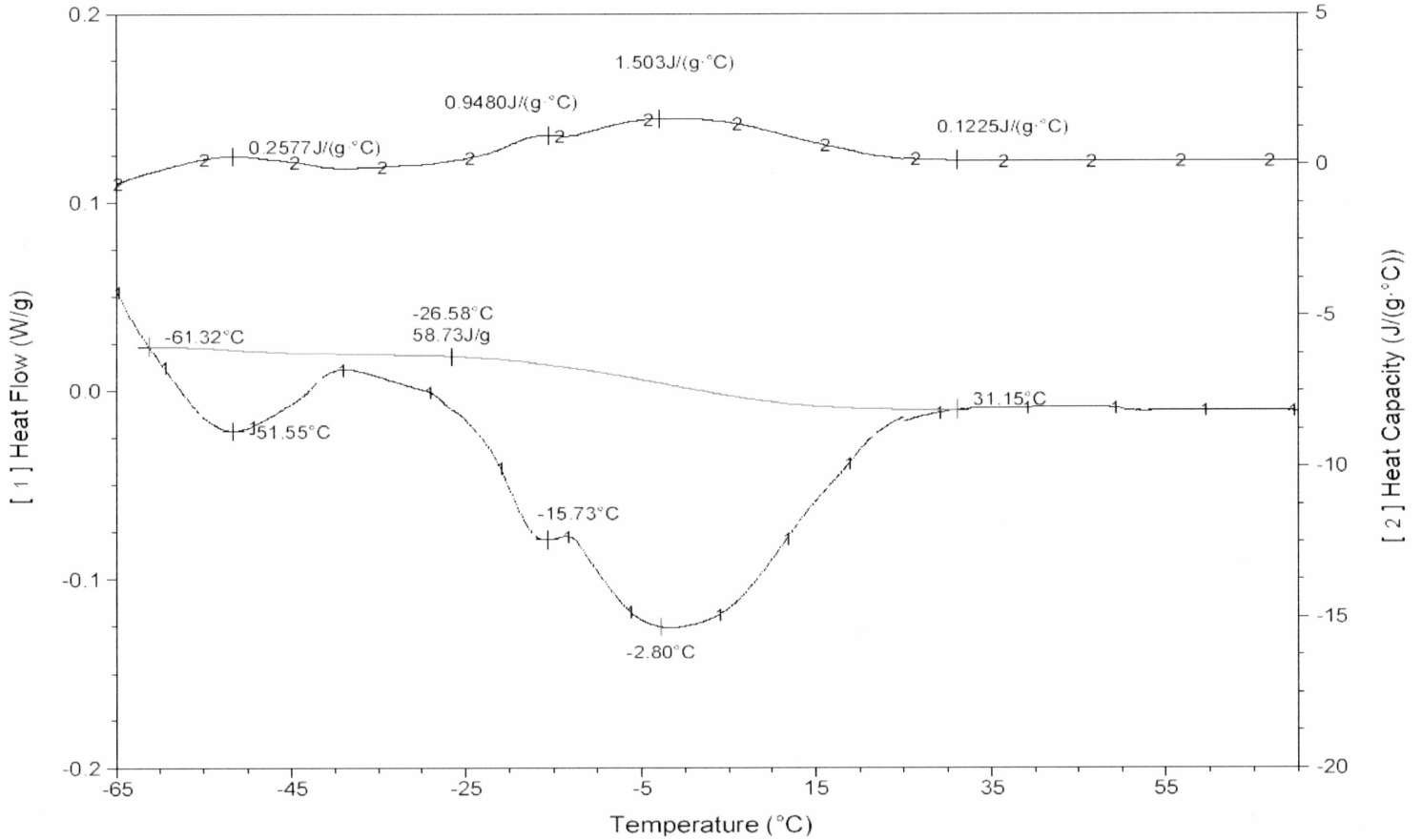

Figure 1.4 Representative DSC thermogram of unpurified salmon oil with heat flow on the left axis (1) and heat capacity (2) on the right axis.

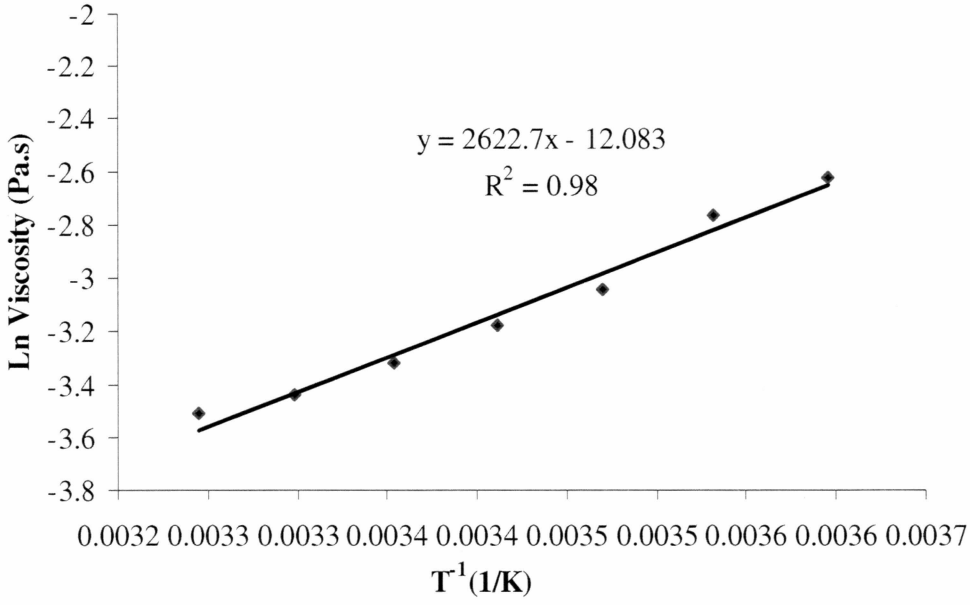

Figure 1.5 The Arrhenius plot for apparent viscosity of the unpurified salmon oil.

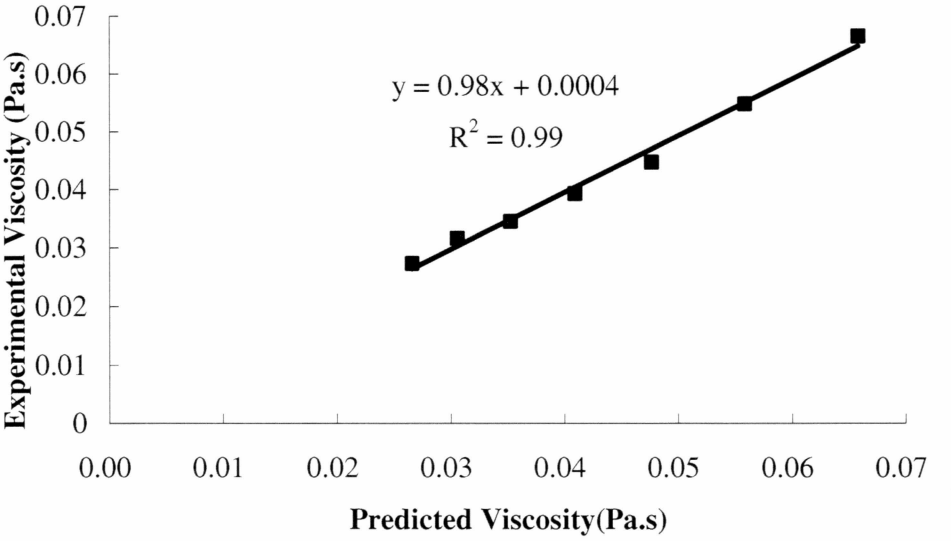

Figure 1.6 Predicted apparent viscosity vs experimental viscosity of the unpurified salmon oil from the Arrhenius plot.

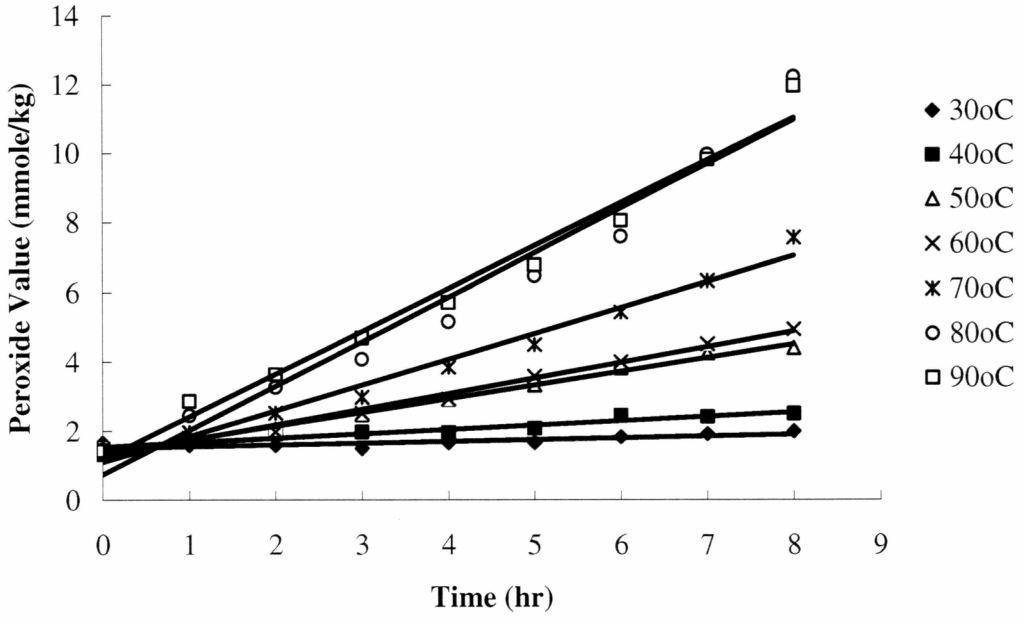

Figure 1.7 Effect of time on peroxide formation in the unpurified salmon oil at different temperatures.

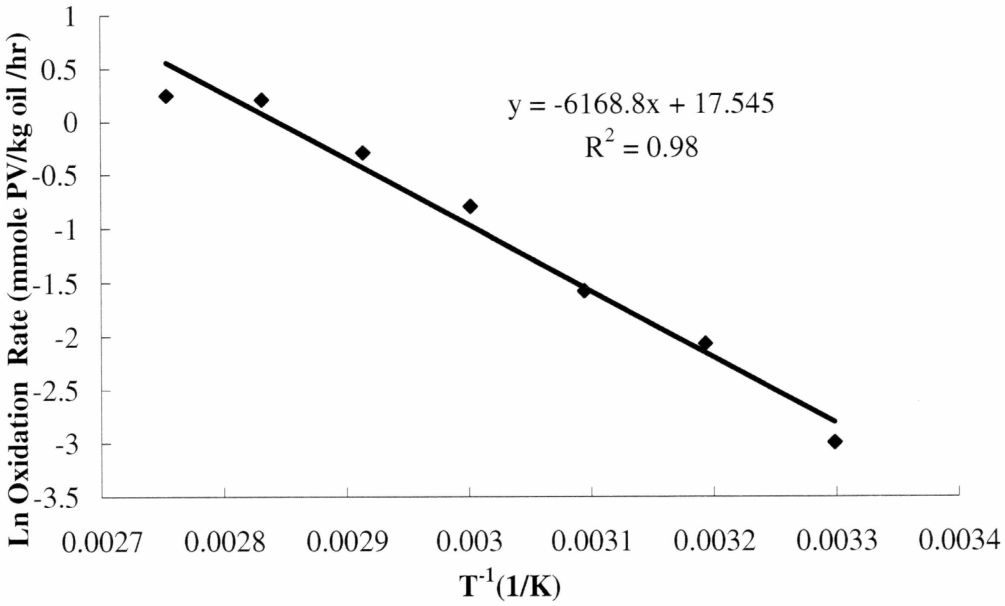

Figure 1.8 The Arrhenius plot for the peroxide values of the unpurified salmon oil.

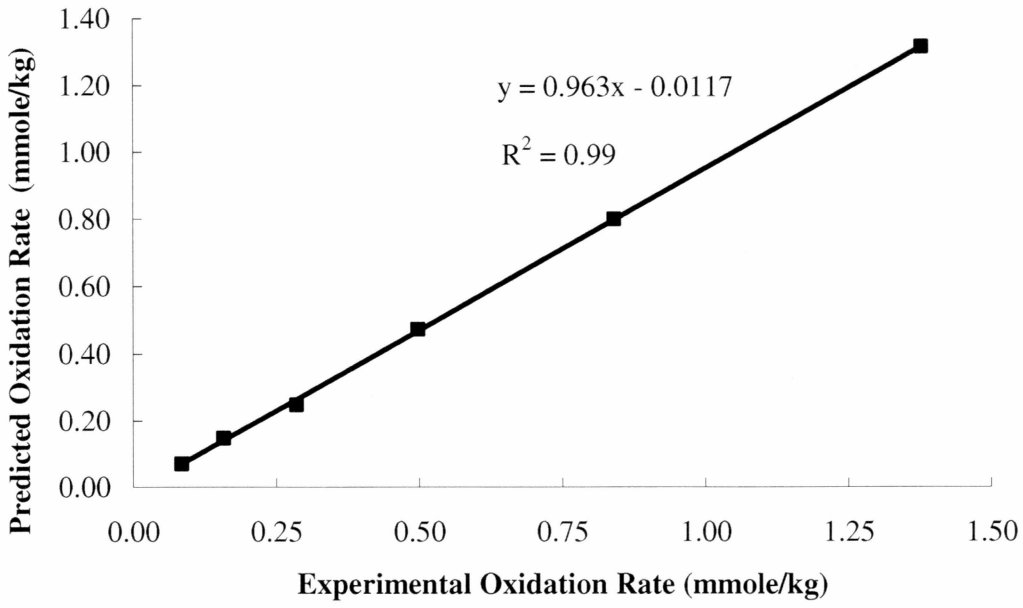

Figure 1.9 Predicted lipid oxidation rate from the Arrhenius plot vs the experimental oxidation rate of the unpurified salmon oil.

Table 1.1 Color, density, specific gravity, water activity, PV and FFA of unpurified salmon oil.

Color L*	26.95±0.16
Color a*	4.24±0.05
Color b*	8.65±0.36
Chroma	9.64±0.33
Hue angle	28.07±1.13
Water activity (a_w)	0.44±0.02
Bulk density (g/mL)	0.91±0.00
Specific gravity[a]	0.92±0.00
PV (mmole/kg)	2.35±0.09
FFA (%)[b]	3.5±0.1

Values are means ± S.D. of 3 determinations.
[a]Specific gravity was measured at 20 ± 1°C. [b]The percentage of free fatty acids was calculated as oleic oil equivalents.

Table 1.2 Apparent viscosity at different temperatures.

Temperature(°C)	n	K (Pa.s ^{n})	Apparent Viscosity (Pa.s)
5	0.88±0.02^{a}	0.148±0.016^{a}	0.071±0.001^{a}
10	0.85±0.05^{ab}	0.132±0.022^{ab}	0.063±0.001^{b}
15	0.86±0.01^{ab}	0.110±0.010^{bc}	0.048±0.001^{c}
20	0.84±0.00^{ab}	0.108±0.004^{bc}	0.042±0.001^{d}
25	0.82±0.01^{ab}	0.107±0.006^{bc}	0.036±0.001^{e}
30	0.80±0.01^{b}	0.105±0.010^{bc}	0.032±0.000^{f}
35	0.80±0.01^{b}	0.097±0.006^{c}	0.030±0.000^{g}
E_a(J.mol^{-1})			21803.04±373.01
μ_∞			5.70E-06±7.65E-07

Values are means ± S.D. of 3 determinations.
$^{a-g}$Means with the same superscript letter in each row are not significantly different (P>0.05).
n = flow behavior index; K = consistency index; Ea = activation energy; μ_∞ = the frequency factor.

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Chapter 2

Purifying Salmon Oil Using Adsorption, Neutralization, and a Combined Neutralization and Adsorption Process

Abstract

The performance of activated earth and/or chitosan as an adsorbent to remove free fatty acids (FFA) and peroxides from the unpurified salmon oil was evaluated. The unpurified salmon oil was purified using three methods included activated earth adsorption process, neutralization process, and combined neutralization and activated earth adsorption processes. The purified salmon oil samples were evaluated for FFA, peroxide values (PV), minerals, color, tocopherols, moisture content, insoluble impurities, and water activity. Neither chitosan nor the activated earth adsorption process was effective in removing FFA from the salmon oil. Neutralized oil had a higher intraparticular diffusion coefficient than the unpurified salmon oil for adsorbing peroxides. FFA of unpurified salmon oil was 3.5% and was significantly reduced ($P<0.05$) to 0.12% by neutralization. No significant reduction of tocopherols content of the oil was observed in any of the three purification processes. After the adsorption process, PV of neutralized oil had decreased from 2.4 to 1.5mmole/kg. All three purification process increased the lightness (L*) and decreased the redness (a*) and reduced mineral, insoluble impurities, moisture content, and water activity of the salmon oil. This study demonstrated that the combined process was more effective in reducing FFA, peroxides, and moisture content than either the activated earth adsorption or neutralization purification processes alone.

Introduction

Large amounts of salmon byproducts are produced in Alaska every year. It is estimated that around 99,000 metric tons of salmon byproducts were produced out of 331,798 metric tons of salmon harvested in Alaska in year 2006 (ADFG, 2007). These salmon byproducts include salmon heads, skin, and viscera. Producing and purifying fish oil from salmon byproducts for the growing fish oil market can benefit the fishing industry in Alaska.

The unpurified salmon oil contains free fatty acids, primary oxidation products, minerals, pigments, moisture, phospholipids, and insoluble impurities that reduce the oil quality. Removal of impurities from unpurified salmon oil is very important to producing purified oil with desirable and acceptable shelf life. These components must be removed as soon as possible from the unpurified oil to avoid negative effects on the oil quality. Designing purification steps to remove these impurities is important to increasing the commercial value of the oils.

Neutralization and adsorption processes can be used to remove most of the impurities that are present in the unpurified salmon oil. Neutralization is a process designed to remove free fatty acids (FFA) from unpurified oil using caustic soda. The adsorption process for oil purification is a process to remove trace metals, pigments, pigment-breakdown products, and primary oxidation products such as aldehydes and ketones (Sathivel & Prinyawiwatkul, 2004; Proctor and Toro-Vazquez, 1996; Miki, 1991). The adsorption process involves the mass transfer of adsorbates from the liquid phase to the adsorbent surface until an isotherm equilibrium is reached (McCabe et al., 1985). The effects of neutralization and adsorption processes have not yet been reported for salmon oil. Therefore, this study provides valuable new

information for the efficient production of salmon oil for human consumption.

The objectives of this study were: (1) to determine the performance of activated earth or chitosan as an adsorbent to remove FFA and peroxides from the unpurified salmon oil (UPO), (2) to purify salmon oil using three methods including the activated earth adsorption process, neutralization process, and combined neutralization and activated earth adsorption processes, (3) to evaluate the adsorption kinetics using activated earth as an adsorbent to remove peroxides from the UPO and neutralized salmon oil (NO), and (4) to analyze PV, FFA, minerals, color, tocopherols, moisture content, insoluble impurities, water activity, and thermal properties of UPO, activated earth adsorbed oil (AEAO), NO, and neutralized and activated earth adsorbed oil (NAEAO).

Material and Methods

Salmon Oil Production

Unpurified salmon oil was produced from processing salmon byproducts including viscera, heads, skins, frame, and discarded fish obtained from a large commercial plant in Alaska. The byproducts were held at the fish processing plants at 8-14°C for 2-4 hours before being transported to the fish meal plants, where they were stored at 10-14°C for 4-48 hours before further processed into fish oil and fish meal. The byproducts were ground and cooked for about 20 min at 95°C. The heated fish byproducts were then mechanically dewatered in a screw press, which subsequently produced press cake and press liquor. The press liquor was clarified using a decanter to remove suspended solids and then the clarified liquor was centrifuged to separate the oil and aqueous fraction. The resulting unpurified oil was

collected from the fish meal plant and stored at -40°C until used at the University of Alaska Fairbanks, Fishery Industrial Technology Center, located in Kodiak, Alaska.

Purifying Salmon Oil

The UPO was purified using three methods including (1) the batch adsorption process, (2) the neutralization process, and (3) the combined neutralization and adsorption process. The activated earth adsorbed oil refers to oil that has been purified using activated earth adsorption. Neutralized oil refers to the oil that has been purified by neutralization. And neutralized and activated earth adsorbed oil refers to oil that has been sequentially neutralized and further purified by activated earth adsorption.

Batch Adsorption Process

Activated earth was obtained from the American Oil Chemists' Society (AOCS) (Champaign, IL). Shrimp chitosan with high viscosity (Vanson Inc., Redmond, WA) was used in this study. The batch adsorption study was conducted in glass containers. Thirty grams of unpurified salmon oil was placed into each glass container and 1.5 g of an adsorbent (activated earth or chitosan) was added separately. The adsorption reaction was carried out with constant agitation using a magnetic stirrer at 22 ± 1°C. Experiments were repeated three times. The oil samples were removed for analysis at 0, 15, 30, 45, 60, 75 and 90-min interval for PV, FFA, color, and water activity. Three additional batches of AEAO were produced as above with a 60-min adsorption time using activated earth. These samples were analyzed for PV, FFA, water activity, minerals, tocopherols profile, insoluble impurities, moisture

content, viscosity, and thermal properties.

Neutralization

The UPO was neutralized according to AOCS Official Method Ca 9b-52 (1998). Sodium hydroxide (12.6 g of 9.5% NaOH solution) was added to 100g of unpurified oil and the mixture was heated to 65°C for 30 min with stirring. The sample was then cooled to room temperature and left undisturbed for 6 hours. After centrifuged at 2,560 g for 10 min, the oil was decanted from the precipitated soap. Fifty mL of demineralized water was added to wash out any remaining soap by centrifuging at 2,560 g for 10 min. Oil was washed three times. Three batches of neutralized oil were produced and analyzed for PV, FFA, water activity, minerals, tocopherols profile, insoluble impurities, moisture content, viscosity, and thermal properties.

A Combined Neutralization and Adsorption Process

The neutralized oil was further purified using activated earth in a batch absorption process at 20°C for 90 min. Samples were taken at 0, 15, 30, 45, 60, 75 and 90-min interval for analysis of PV, FFA, color, and water activity. Three additional batches of NAEAO were produced using activated earth after a 60-min adsorption time and were used for analysis of PV, FFA, water activity, minerals, tocopherols profile, insoluble impurities, moisture content, viscosity, and thermal properties.

PV, FFA, Color, and Water Activity Analysis

The peroxide value (PV) of the salmon oil samples was measured by titration according to AOAC (1999). Free fatty acids (FFA) were determined using the titration procedure according to AOCS (1998). The percentage of FFA was expressed as oleic acid equivalents. Color analysis of salmon oil was measured in triplicate using a Minolta Chromameter (Model CR-300, Minolta Co., Ltd, Osaka, Japan). The data was reported in the CIELAB color scales (L*, a* and b* values). Water activity was measured using an AqualLab water activity meter (Model Series 3 TE, Decagon Devices, Inc., Pullman, WA) at 20 ± 1°C.

Adsorption Kinetics of PV for Producing AEAO and NAEAO

The external film mass transfer coefficient, K_sA, (mL min^{-1}) was calculated from Equation 2.1 according to Kadirvelu et al. (2000).

$$-In\left(\frac{C}{C_o}\right) = KsA\frac{t}{V} \qquad (2.1)$$

where C is the concentration of PV (mmole/kg) at time t; C_0 is the initial PV concentration (mmole/kg); t is the time (min); V is the volume (mL) of the oil sample.

The intraparticular diffusion coefficient K_w (μmole ml^{-1} $min^{-0.5}$) was calculated from Equation 2.2 according to Kadirvelu et al. (2000).

$$\frac{m}{V}q = K_w t^{0.5} \qquad (2.2)$$

where q (μMole g^{-1}) is the adsorption capacity at time t.

The adsorption capacity was calculated as $q = (C_0\text{-}Ct)V/W$, where C_0 = initial PV concentration (mmole/kg), Ct = concentration of PV (mmole/kg) at time t (min), V

= volume of oil (mL), W = m = weight of adsorbent (g). The adsorption capacity at saturation was calculated as $q_s = (C_0\text{-}Cs)V/ W$, where C_0 = an initial PV concentration (mmole/kg), Cs = concentration of PV (mmole/kg) at saturation, V = volume of oil (mL), W = weight of adsorbent (g).

Mineral, Tocopherols, Insoluble Impurities, and Moisture Content of UPO, AEAO, NO, and NAEAO Oils

Mineral, tocopherols, insoluble impurities, and moisture content of oil samples were determined by the POS Pilot Plant Corp Laboratory, Saskatchewan, Canada. Mineral content of salmon oil samples was determined according to AOCS Ca17-01 and AOCS Ca 20-99 (1998) and reported as ppm. Levels of tocopherols in the oil samples (alpha tocopherol; beta tocopherol; gamma tocopherol, and delta tocopherol) were determined according to AOCS Ce8-89 (1998) and reported as mg/g of oil. Insoluble impurities of salmon oil samples were measured according to AOCS Ca-46 (1998). Moisture content of salmon oil samples was measured using the Karl Fisher Titration Method (AOAC Method 984.20 (1999)).

Rheological Analysis

An Advanced Rheometer (Model AR2000; TA Instruments, Ltd, New Castle, DE) fitted with a cone plate geometry (acrylic plates with a 20-mm diameter, having a 200 μm gap between the two plates) was used to study the rheological properties of the oil samples at different temperatures. Approximately 0.1 gram of the oil sample from UPO, AEAO, NO, or NAEAO was placed in the temperature-controlled parallel plate and allowed to equilibrate to 10, 15, 20, or 25°C. The shear stress was

measured at 10, 15, 20, or 25°C at varying shear rates from 0 to 500 s^{-1}. The mean values of triplicate samples were reported.

Thermal Analysis of UPO, AEAO, NO, and NAEAO Oils

Thermal stability of the salmon oil sample was analyzed using the thermogravimetric analyzer (Model Q50, TA Instruments, New Castle, DE). Approximately 10 mg of the oil sample was added to a platinum pan, the pan was placed in the furnace, and the exact sample weight was determined. The sample was heated to 700°C under air atmosphere at a rate of 5°C/min. Sample weight differences were automatically recorded every 0.5 sec. Collected data were analyzed and plotted using the TA Universal Analyzer Software. The graph was normalized based on the sample weight basis.

The differential scanning calorimetry (DSC) experiments were conducted using a differential scanning calorimeter (Model DSC 2920, TA Instruments, New Castle, DE). Approximately 1-5 mg of the unpurified salmon oil sample was placed in the aluminum sample vessel. The sample vessel was then placed on the sample platform while an empty aluminum vessel was placed on the reference platform. To determine the phase transition of the unpurified salmon oil, a linear heating rate of 5°C/min over a temperature range of -75 to 100°C was used. The thermogram peak was used to provide an estimate of enthalpy (ΔH). The thermogram peak points were used to determine the melting points. The TA Instrument Software was used to calculate the specific heat capacity from the DSC transition curve.

Statistical Analysis

Means and deviations of the data collected were reported. Multiple comparison was performed at the significant level of $P<0.05$ using SAS version 8.2 (SAS Institute Inc., 2002). Tukey's studentized range tests were performed to detect significant differences among the different treatments.

Results and Discussion

Batch Adsorption Process

Activated earth effectively adsorbed primary oxidation products better than chitosan (Figure 2.1). The initial PV of unpurified salmon oil was 2.4 mmole per kilogram of fish oil (Figure 2.1). The PV value indicated the amount of primary oxidation products adsorbed onto the activated earth increased with contact time (Figure 2.1). Significant differences between the activated earth adsorbed oil and chitosan adsorbed oil were seen after 15 min. After 60 min of adsorption using activated earth, PV was reduced to 1.50 mmole per kilogram of fish oil. The adsorption properties of activated earth on the primary oxidization products may be related to hydrogen bonding (Brown & Snyder, 1985; Hau & Nawar, 1985); competition for adsorption sites (Morgan et al, 1985); electrostatic field strength, and intraparticles diffusion of molecules (Taylor & Ungermann, 1984); and hydrophobic interaction (Ruthven, 1984). In this study, chitosan was not effective as an adsorbent to adsorb primary oxidation products.

Neither activated earth nor chitosan was effective in reducing FFA from the unpurified salmon oil (Figure 2.2). Possible explanations include the presence of

other impurities such as minerals and protein in the fish oil, or the viscosity of the oil. Proctor & Palaniappan (1990) reported that processed rice hull ash could be used as an adsorbent to adsorb FFA from soy oil diluted with hexane. And Palaniappan & Protor (2005) stated the dilution was an important component, which may increase external mass transfer between adsorbent and adsorbate. However, the oil was not diluted with solvent in this study. The activated earth adsorption reduced the primary oxidation production in the UPO but had not reduced the FFA of the oil. It was somewhat surprising that chitosan, which has a number of functional groups, did not removed FFA and primary oxidation products from the UPO.

The initial L*, a*, and b* values of the unpurified salmon oil were, respectively, 27.0, 4.2, and 8.7 (Table 2.1). Chitosan and activated earth effectively increased the lightness of the oil (Tables 2.1 and 2.2). After 90 min adsorption, the L* values increased to 45.4 and 46.4, respectively, in chitosan and activated earth adsorption treatments. Both chitosan and activated earth adsorptions affected color redness (a*) and yellowness (b*) of the salmon oil. The a* value decreased with the increase in adsorption time. All oils with negative a* values indicating a slight green color indicate that a reduction in red pigment occurred during the adsorption process. The coloration of salmon oil is due in part to carotenoid pigments, notably astaxanthin and canthaxanthin. And carotenoids pigments have been shown to be adsorbed from oil by adsorbents (Brekke, 1980). The b* value of the oil increased with the increase in adsorption time and the salmon oil was becoming more yellowish color. Both chitosan and activated earth processing of oil resulted in clear yellowish salmon oils.

Table 2.3 shows the relationship between water activity and contact time. Initial water activity of unpurified oil was 0.43 and it was reduced after 90 min of

adsorption to 0.27, 0.32 for chitosan, and activated earth, respectively. Both chitosan and activated earth are effective in reducing water activity in salmon oil.

Characterization of NO, AEAO, and NAEAO

FFA are regarded as major impurities in the salmon oil. It is very important to maximize the removal of FFA. The initial FFA content of unpurified salmon oil was 3.5% and this was reduced to 0.12% by neutralization (Table 2.4). An acceptable level of FFA in purified fish oil has been reported to be 0.15% by Young (1986a).

The PV of unpurified salmon oil increased from 2.4 to 4.8 (mmole/kg) during the neutralization process, which confirmed an increase in lipid oxidation occurred as a result of the neutralization process. The neutralization process elevated the oil temperature to 65°C for 30 minutes, which may contribute to lipid oxidation in the neutralized oil. Lipid oxidation is a major problem during extraction, purification, and storage of fish oil. And PV is a good indicator of lipid oxidation. Sathivel et al. (2007) reported changes in PV of the unpurified fish oil as a function of time and temperature.

Activated earth adsorption on the neutralized salmon oil showed a decrease in PV with increased adsorption time (Table 2.4). This indicates that activated earth was effective in adsorbing the primary oxidation products. After 60 min of adsorption, the activated earth treatment was saturated with primary oxidation products and the PV of NO was reduced to 2.9 mmole per kilogram of fish oil. Activated earth adsorption had no additional effect on adsorbing FFA from the NO with increasing adsorption time.

The neutralized oil was lighter (L* = 38) and more yellowish (b* = 32) in color than UPO. NO had similar redness (a* = 0.42) color as UPO, which indicated that neutralization process may not have significantly removed carotenoids pigments (Table 2.4). However, the activated earth adsorption process improved the lightness of the NO sample. NO had lower L* value (38.0) than the NAEAO samples. The a* value of NO decreased with increased activated earth adsorption time, which indicated reduction in red pigment during the adsorption process. The b* value of the neutralized oil generally decreased with increased activated earth adsorption time as the salmon oil was becoming lighter, colorless, and transparent.

Adsorption Kinetics and Mass Transfer of PV

Figure 2.3 and Table 2.5 show the PV changes during the activated earth adsorption in UPO and NO samples. Comparisons of kinetic parameters of activated earth adsorption in UPO and NO salmon oil are given in Table 2.5. The amount of peroxides adsorbed per g of activated earth was expressed as a function of time (Figure 2.3). The adsorption efficiency of the activated earth increased sharply for both oils up to 60 min. The maximum amount of peroxides adsorbed per g of activated earth was 17.3 and 38.3 μmole/g, respectively, in UPO and NO (Figure 2.3). The *KsA* values are affected by the concentration gradient of the adsorbate between the fluid phase and the adsorbent surface, temperature, viscosity, and pH (Weber, 1985). Similar *KsA* values were observed for activated earth adsorption process in UPO and NO salmon oils (Table 2.5). Activated earth has higher *Kw* value ($P<0.05$) in NO sample than in UPO sample.

Mineral, Tocopherols, Insoluble Impurities, and Moisture Content of UPO, AEAO, NO, and NAEAO Oils

Table 2.6 lists the mineral contents of UPO, AEAO, NO, and NAEAO oil samples. Mg, Ca, Fe, and P were the most abundant minerals found in unpurified salmon oil. UPO contained a high amount of P (43.1 ppm), which was reduced to 10.6 ppm, 0.32 ppm, and 0.40 ppm after the activated earth adsorption, neutralization, and the combined process, respectively. The phosphorus present in salmon oil may be attributed to the phospholipids in the oil sample and calcium-phosphate complexes (Young, 1986a).

The levels of Ca (45.8 ppm) and Mg (13.2 ppm) in the UPO were reduced after the activated earth adsorption; however, neutralization and the combined process were more effective in reducing these minerals than that alone of activated earth adsorption. UPO had copper (0.07 ppm) and iron (4.21 ppm) contents below the acceptable level for copper of 0.23 ppm and iron of 8 ppm (Young, 1986a; Bimbo, 1998). The level of copper and iron were reduced during the adsorption, neutralization, and the combined processes. Metal, such as copper and iron, present in the oil catalyze oxidation (Young, 1986b); however, the PV value of UPO was lower than the acceptable level of 3 mmole/kg (Young, 1986b).

Lunde (1971) reported that unpurified edible oils are expected to contain a certain amount of minerals because phospholipids are reported to bind minerals in the oil. Minerals such as phosphorous, iron, magnesium and calcium in the oil can be reduced to trace levels by neutralization (Hvolby, 1989), which may also remove phospholipids during the washing step in neutralization process. In addition, most of minerals and metals precipitated with the soap as saponification occurred during

neutralization. Neutralization increased the sodium content in the oil from 3.09 to 3.73 ppm because of the added sodium hydroxide; however, both activated adsorption and combined processes reduced the sodium content in the oil.

Minerals, such as arsenic, mercury, lead, and selenium, present in the UPO can negatively affect human health. The unpurified salmon oil had trace level of mercury, lead, and selenium, while arsenic content was higher than an acceptable level of 3 ppm. Activated earth adsorption at 60 min reduced arsenic concentrations from 6.78 ppm to trace level (<0.2 ppm). The adsorbent-adsorbate interaction potential largely depends on the pore size and geometry of the adsorbents (Yang, 2003). Activated earth has a desirable fine pore shape, which provides a large surface area for adsorbing the minerals.

Tocopherols play a role as a vitamin and natural antioxidant. The amounts of tocopherols in the oils are listed in Table 2.6. Total tocopherol content of the UPO (0.36 mg/g) was slightly higher than the oils purified by activated earth adsorption (0.3 mg/g), neutralization (0.3 mg/g), and the combined purified method (0.29 mg/g).

All three purification processes effectively reduced initial insoluble impurities in the UPO from 0.02% to less than0.01%. The initial moisture content of the unpurified fish oil was 0.28%, which reduced to 0.11%, 0.11%, and 0.06%, respectively, for activated earth adsorption, neutralization, and the combined process.

Apparent Viscosity of UPO, AEAO, NO, and NAEAO Oils

Apparent viscosity of UPO was significantly ($P< 0.05$) higher than those of AEAO and NAEAO at 10, 15, 20, and 25 ^{o}C (Table 2.7). The NAEAO samples had lower apparent viscosity ($P< 0.05$) at 10 to 15^{o}C than UPO, AEAO, and NO samples.

Unpurified salmon oil contained large amount of impurities including Mg, Ca, Fe, P, free fatty acids, and peroxides, insoluble impurities, and moisture (Table 2.6) that are highly interactive with the oil (Wiedermann, 1981). Sathivel et al. (2003b) reported on changes of fish oil rheological properties during the purification processes. According to Teeter & Cowan (1956), the interface between oil and impurities may be attributed to the development of an aggregated colloidal dispersion system, which often shows higher viscosity in the unpurified oil.

Thermal Analysis of UPO, AEAO, NO, and NAEAO Oils

The thermal degradation of UPO, AEAO, NO, and NAEAO is given in Figure 2.4. Regardless of the purification methods, weight loss of oils increased with increased heating temperature between 200 to 500°C. At 550°C, NAEAO sample was completely decomposed, while UPO, AEAO, and NO samples retained 0.2, 0.2, and 0.1% of their initial weight, respectively. According to the TG curves (Figure 2.4), the thermal stability of the oil samples are as follow: UPO > NO > AEAO > NAEAO. The presence of impurities in the oil samples reduces heat transfer to unpurified oils; therefore, less energy available to evaporate the volatiles. Sathivel et al. (2003a) reported that the weight loss of oils due to thermal decomposition is higher in purified oils than those of unpurified oils. In this study, NAEAO oil had less relative resistance to thermal decomposition at 550°C, which indicates that TG analysis may be useful in evaluating the quality of fish oils.

The DSC thermograms (Figure 2.5) show differences in melting points of UPO, AEAO, NO, and NAEO samples. Sharper melting point peaks were observed for NAEAO compared to the other oil samples. Unpurified oil contains impurities

such as free fatty acids, aldehydes, ketones, water, minerals, and insoluble impurities, which are removed during adsorption (Young, 1978; Richardson, 1978). It can be clearly seen from Figure 2.5 that melting point peaks of NAEAO were sharper after the combined purification process, which is possibly due to the removal of impurities. These results support the use of DSC to evaluate fish oil quality.

Conclusion

The results indicated that activated earth had a good ability to adsorb peroxides, minerals, moistures, and insoluble impurities of unpurified salmon oil. Neither chitosan nor activated earth was effective in removing FFA from unpurified salmon oil in this study. FFA content of the oil was significantly reduced by the neutralization process; however, PV increased. The neutralization process also reduced minerals, insoluble impurities, and moisture content of the oil. The combined method was more effective in reducing PV and FFA from the salmon oil than that of either the activated earth adsorption or neutralization process. All three purification processes increased the lightness of the oil, while decreasing the redness of the oil. The tocopherols value was minimally affected by the three purification processes. NAEAO oil samples had lower apparent viscosity at 10, 15, and 25°C than UPO, AEAO, and NO oils samples. NAEAO oil sample was completely decomposed at 550°C. The DSC thermogram of NAEAO had narrower and sharper melting point peaks than other samples, indicating fewer impurities were left in the oil sample of this treatment.

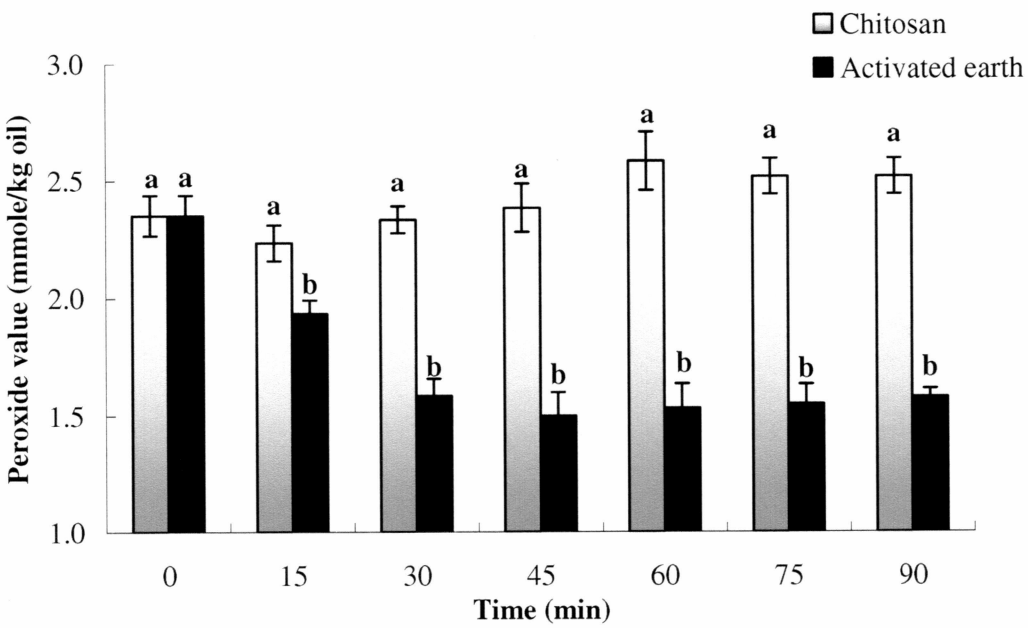

Figure 2.1 Peroxide values of salmon oil at different adsorption time intervals of chitosan and activated earth treatments.
Bars are means ± S.D. of 3 determinations. Means with the same letter at each time are not significantly different ($P>0.05$).

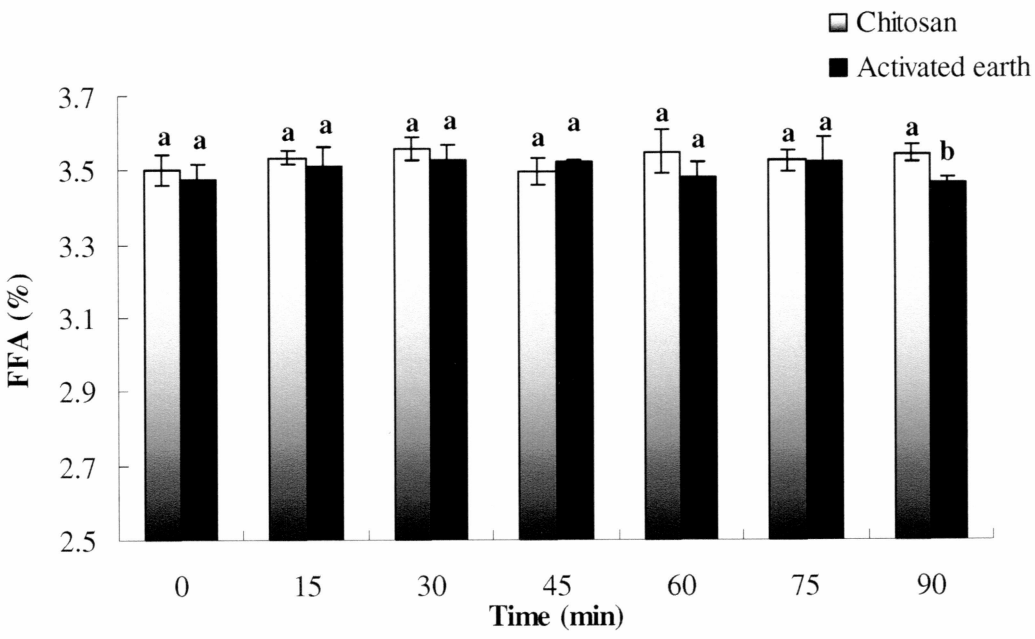

Figure 2.2 Free fatty acids (FFA) of salmon oil at different adsorption time intervals.

Bars are means ± S.D. of 3 determinations. Means with the same letter at each time are not significantly different ($P>0.05$).

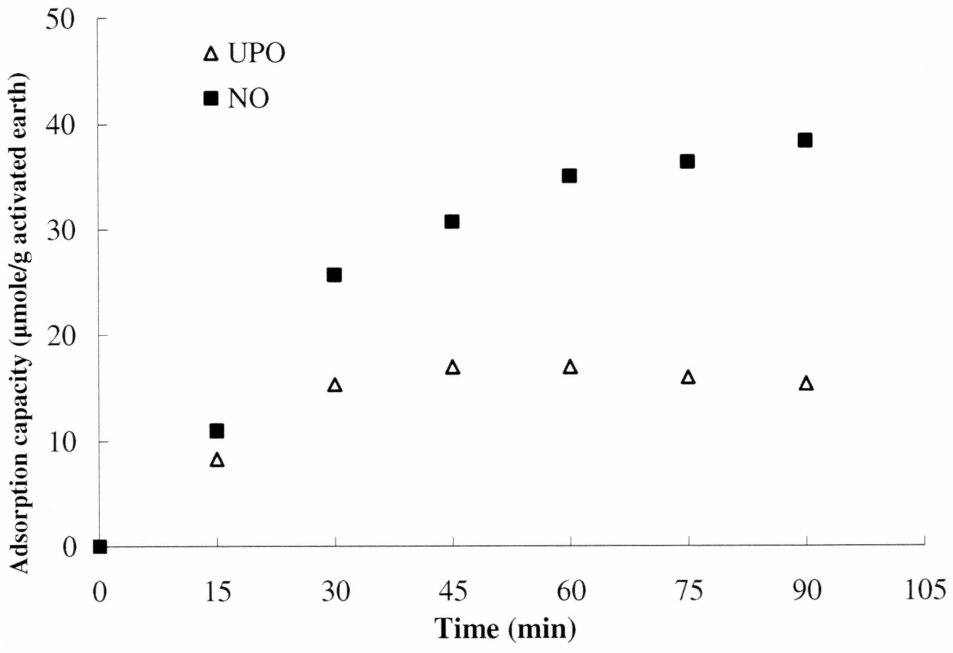

Figure 2.3 Activated earth adsorption capacity of peroxides at different adsorption time in UPO and NO.
UPO = unpurified salmon oil; NO = neutralized oil. Values are means of 3 determinations.

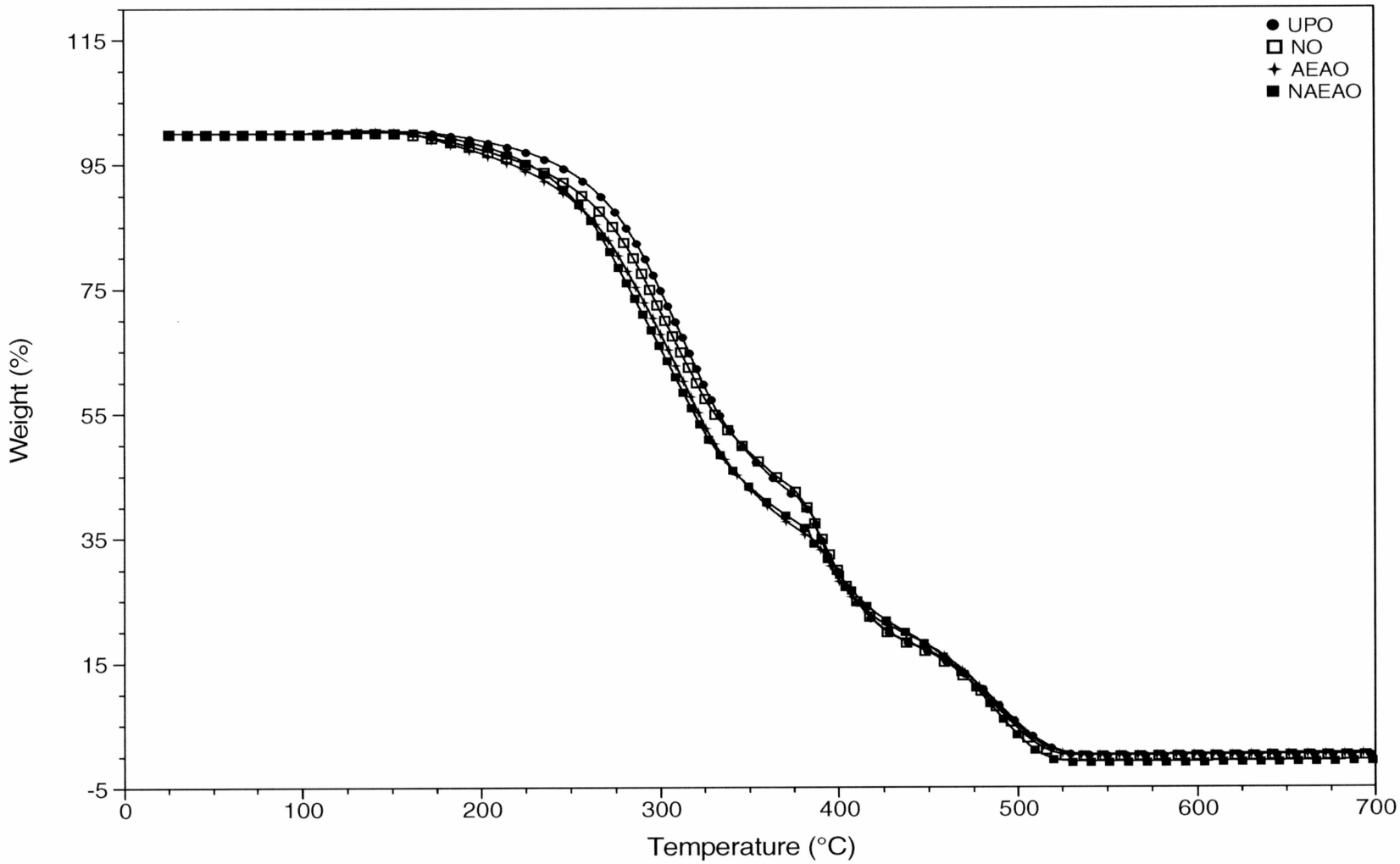

Figure 2.4 Representative thermal degradation of UPO, AEAO, NO, and NAEAO oils over the temperature range of 20 to 700°C. UPO = unpurified oil; NO = neutralized oil; AEAO = activated earth adsorbed oil; NAEAO = neutralized and activated earth adsorbed oil.

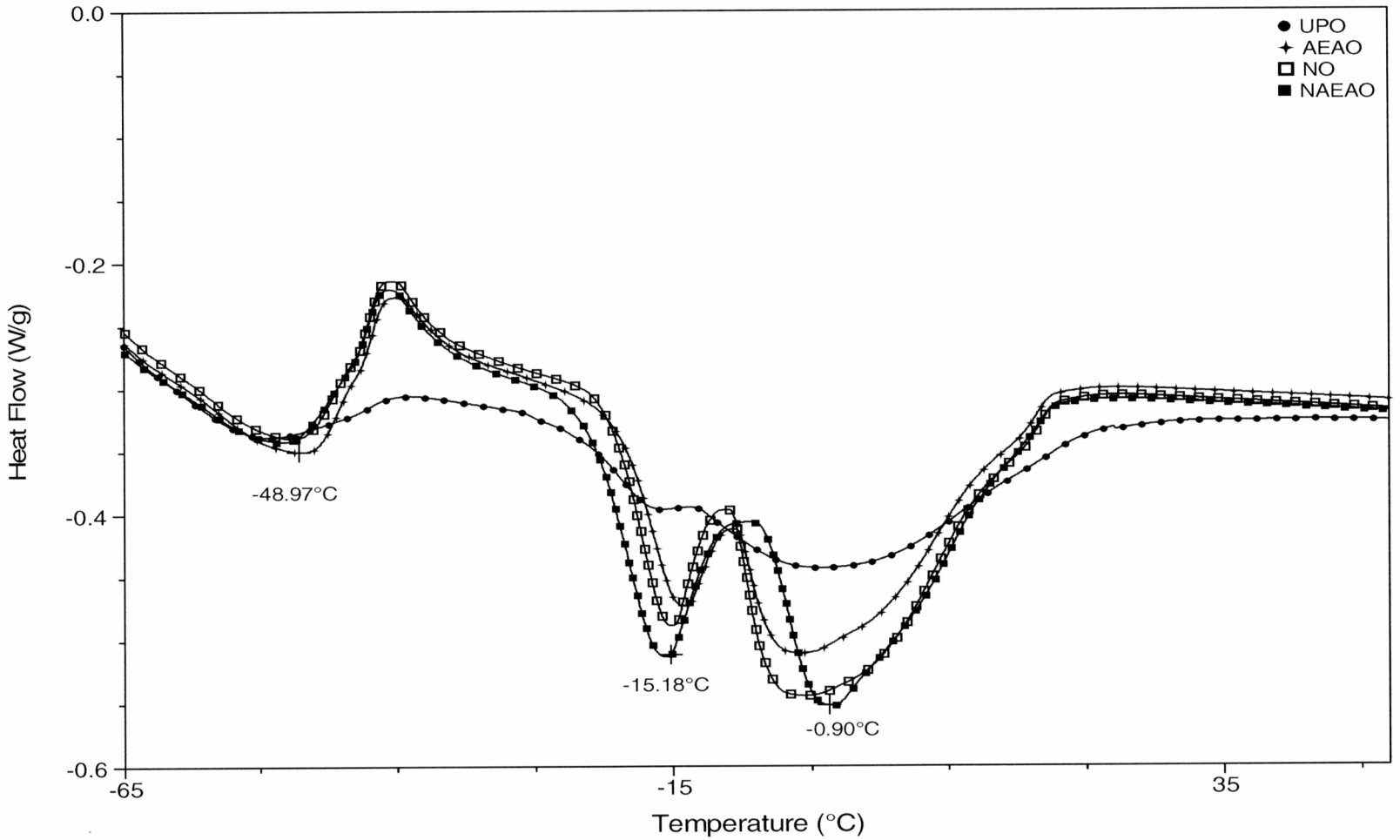

Figure 2.5 Representative DSC thermogram of UPO, AEAO, NO, and NAEAO oils.

UPO = unpurified oil; AEAO = activated earth adsorbed oil; NO = neutralized oil; NAEAO = neutralized and activated earth adsorbed oil.

Table 2.1 Color L*a*b* values of salmon oil samples taken at different adsorption time intervals for chitosan as the adsorbent.

Time (min)	L*	a*	b*
0	27.0 ± 0.2^{d}	4.2 ± 0.1^{a}	8.7 ± 0.4^{e}
15	34.6 ± 3.9^{c}	4.0 ± 0.1^{b}	13.7 ± 1.2^{d}
30	41.2 ± 1.2^{ab}	2.4 ± 0.0^{c}	22.2 ± 0.4^{c}
45	40.4 ± 1.3^{b}	$2.3\pm0.^{1c}$	29.5 ± 0.5^{b}
60	42.0 ± 1.7^{ab}	2.4 ± 0.1^{c}	33.5 ± 1.4^{a}
75	45.7 ± 0.5^{ab}	-0.0 ± 0.1^{d}	34.7 ± 0.7^{a}
90	45.4 ± 1.3^{a}	-0.1 ± 0.0^{d}	34.1 ± 1.7^{a}

Values are means ± S.D. of 3 determinations. Means with the same letter in each column are not significantly different ($P>0.05$).

Table 2.2 Color L*a*b* values of salmon oil samples taken at different adsorption time intervals for activated earth as an adsorbent.

Time (min)	L*	a*	b*
0	27.0 ± 0.2^{c}	4.2 ± 0.1^{a}	8.7 ± 0.4^{c}
15	42.1 ± 0.2^{b}	-1.5 ± 0.0^{b}	26.5 ± 0.4^{a}
30	43.1 ± 0.2^{b}	-2.6 ± 0.0^{d}	24.4 ± 0.1^{ab}
45	43.1 ± 0.8^{b}	-2.2 ± 0.1^{c}	26.2 ± 0.7^{ab}
60	$43.1\pm0.^{2b}$	-2.6 ± 0.0^{d}	24.4 ± 0.1^{ab}
75	45.4 ± 1.0^{a}	-3.3 ± 0.2^{e}	24.0 ± 1.3^{b}
90	46.4 ± 1.0^{a}	-3.3 ± 0.2^{e}	24.1 ± 1.7^{b}

Values are means ± S.D. of 3 determinations. Means with the same letter in each column are not significantly different ($P>0.05$).

Table 2.3 Water activity of salmon oil samples taken at different adsorption time intervals.

Time (min)	Activated earth	Chitosan
0	0.43 ± 0.03^{a}	0.43 ± 0.03^{a}
15	0.39 ± 0.01^{a}	0.38 ± 0.01^{ab}
30	0.38 ± 0.02^{a}	0.36 ± 0.02^{bc}
45	0.29 ± 0.01^{b}	0.35 ± 0.01^{bc}
60	0.29 ± 0.01^{b}	0.35 ± 0.01^{bc}
75	0.28 ± 0.04^{b}	0.32 ± 0.01^{c}
90	0.27 ± 0.03^{b}	0.32 ± 0.02^{c}

Values are means ± S.D. of 3 determinations. Means with the same letter in each column are not significantly different ($P>0.05$).

Table 2.4 Effects of UPO, NO, and NAEAO treatments on salmon oil PV, FFA, color, and water activity values.

Oil samples[b]	PV (mmole/kg)	FFA (%)	Color			a_w
			L*	a*	b*	
UPO	2.35±0.09[e]	3.48±0.04[a]	27.0±0.2[e]	4.2±0.1[a]	8.7±0.4[e]	0.43±0.03[a]
NO	4.75±0.10[a]	0.12±0.01[b]	38.5±0.8[d]	4.2±0.2[a]	31.5±1.7[a]	0.43±0.01[a]
NAEAO 0 min	4.87±0.13[a]	0.13±0.01[b]	38.0±0.7[d]	4.1±0.1[a]	30.2±1.2[a]	0.41±0.01[a]
NAEAO 15 min	4.20±0.13[b]	0.13±0.01[b]	40.1±0.2[c]	-2.2±0.1[b]	26.0±0.1[b]	0.39±0.02[a]
NAEAO 30 min	3.47±0.06[c]	0.13±0.01[b]	43.7±0.6[b]	-3.0±0.1[c]	27.8±1.0[b]	0.31±0.02[b]
NAEAO 45 min	3.22±0.06[cd]	0.14±0.01[b]	45.3±0.4a[b]	-3.6±0.1[d]	26.2±0.4[b]	0.31±0.01[b]
NAEAO 60 min	3.00±0.10[d]	0.14±0.01[b]	46.1±1.4[a]	-3.8±0.2[d]	20.6±1.1[c]	0.25±0.02[c]
NAEAO 75 min	2.90±0.15[d]	0.14±0.01[b]	45.7±0.6a[b]	-3.6±0.1[d]	17.1±0.5[d]	0.24±0.01[c]
NAEAO 90 min	2.90±0.10[d]	0.14±0.01[b]	46.4±1.4[a]	-3.8±0.2[d]	18.9±0.9[cd]	0.24±0.02[c]

Values are means ± S.D. of 3 determinations. Means with the same letter in each column are not significantly different ($P>0.05$). UPO = unpurified salmon oil; NO = neutralized oil; NAEAO = neutralized activated earth adsorbed oil at 10, 15, 30, 45, 60, 75, 90 min adsorption time.

Table 2.5 Adsorption kinetics coefficients for peroxides during batch adsorption using activated earth in UPO and NO.

Samples	KsA (mL min^{-1})	K_w (μmole ml^{-1} $min^{-0.5}$)	q_s (μmole g^{-1})
UPO	0.36 ± 0.04^a	0.12 ± 0.01^b	17.0 ± 2.0^b
NO	0.33 ± 0.03^a	0.20 ± 0.01^a	38.3 ± 1.5^a

Values are means ± S.D. of 3 determinations. Means with the same letter in each column are not significantly different ($P>0.05$). UPO = unpurified oil; NO = neutralized oil; KsA = external film mass transfer coefficient; K_w = intraparticular diffusion coefficient; q_s = adsorption capacity at saturation.

Table 2.6 Minerals, tocopherols, insoluble impurities, and moisture content of salmon oil samples.

	UPO	AEAO	NO	NAEAO
Calcium (ppm)	45.8	13.8	0.57	0.04
Copper (ppm)	0.07	<0.05	<0.05	<0.05
Iron (ppm)	4.21	1.63	0.03	<0.02
Potassium (ppm)	<0.05	<0.05	<0.05	<0.05
Magnesium (ppm)	13.2	3.25	0.25	0.22
Phosphorus (ppm)	43.1	10.6	0.32	0.40
Sodium (ppm)	3.09	0.91	3.73	<0.02
Zinc (ppm)	0.81	0.18	0.02	<0.02
Arsenic (ppm)	6.78	<0.20	<0.20	<0.20
Cadmium (ppm)	<0.03	<0.03	<0.03	<0.03
Mercury (ppm)	<0.20	<0.20	<0.20	<0.20
Lead (ppm)	<0.20	<0.20	<0.20	<0.20
Selenium (ppm)	<0.50	<0.50	<0.50	<0.50
Alpha Tocopherol (mg/g oil)	0.36	0.30	0.30	0.29
Beta Tocopherol (mg/g oil)	<0.01	<0.01	<0.01	<0.01
Gamma Tocopherol (mg/g oil)	<0.01	<0.01	<0.01	<0.01
Delta Tocopherol (mg/g oil)	<0.01	<0.01	<0.01	<0.01
Total Tocopherols (mg/g oil)	0.36	0.30	0.30	0.29
Insoluble impurities (%)	0.02	<0.01	<0.01	<0.01
Moisture (%)	0.28	0.11	0.11	0.06

UPO = unpurified oil; AEAO = activated earth adsorbed oil; NO = neutralized oil; NAEAO = neutralized and activated earth adsorbed oil.

Table 2.7 Apparent viscosity (Pa·s) of UPO, NO, AEAO, and NAEAO samples at different temperatures.

Samples	10°C	15°C	20°C	25°C
UPO	0.066±0.001[a]	0.054±0.001[a]	0.046±0.001[a]	0.040±0.001[a]
AEAO	0.060±0.001[b]	0.050±0.001[b]	0.041±0.000[b]	0.035±0.001[b]
NO	0.065±0.001[a]	0.055±0.002[a]	0.045±0.001[a]	0.035±0.001[b]
NAEAO	0.056±0.001[c]	0.047±0.001[c]	0.039±0.001[b]	0.030±0.001[c]

Values are means ± S.D. of 3 determinations. Means with the same letter in each column are not significantly different ($P>0.05$). UPO = unpurified oil; AEAO = activated earth adsorbed oil; NO = neutralized oil; NAEAO = neutralized and activated earth adsorbed oil.

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General Conclusions

The salmon industry is one of the largest fishing industries in Alaska. Most wild salmon harvested in Alaska are sold either canned or headed and gutted (H&G). Processing recovery rates for salmon are 65-67% and 72-75%, respectively for canning and for H&G. Over 99,000 metric tons of salmon byproducts are produced, which take up about 27% of the total weight of salmon harvested in 2006. These salmon byproducts include salmon heads, skin, and viscera. Producing and purifying fish oil from salmon byproducts for the growing fish oil market can benefit the whole fish industry in Alaska. Much of the oil in salmon byproducts is found in the head, which contains approximately 15-18% lipid. Salmon oil is an excellent source of omega-3 fatty acids, which are recognized for their great value to human health.

The efficiency and quality of salmon oil production is extremely important to the industry with the increasing demand of fish oil as healthy and functional food. Unpurified salmon oil contains various impurities including free fatty acids (FFA), phospholipids, minerals, crude proteins, moisture, and oxidation products. These impurities must be removed to produce good quality salmon oil for human consumption. To the best of our knowledge, very little or no interest has been paid by the industries to purification of salmon oil. This research is intended to help fill the gaps in the research on purification of salmon oil.

The Master of Science research objectives were (1) to determine the thermal stability, melting point, specific heat capacity, enthalpy, and rheological properties and (2) to determine the effects of temperature on the viscosity and oxidation rates of the salmon oil, (3) to evaluate the performance of activated earth or chitosan as an

adsorbent to remove FFA and peroxides from the unpurified salmon oil, (4) to purify salmon oil using activated earth adsorption process, neutralization process, and combined neutralization and activated earth adsorption processes, (5) to evaluate the adsorption kinetics using activated earth as an adsorbent to remove PV from the unpurified salmon oil and neutralized salmon oil, and (6) to characterize the unpurified salmon oil, activated earth adsorbed oil, neutralized oil, and neutralized and activate earth adsorbed oil for FFA, PV, minerals, color, tocopherols, moisture content, insoluble impurities, thermal properties and viscosity.

The first chapter was devoted to modeling the effects of temperature on the magnitude of viscosity and lipid oxidation rates of unpurified salmon using the Arrhenius equation. The salmon oil melted from – 61.3 to 31.2°C and exhibited non-Newtonian fluid behavior. The predicted viscosity obtained by the Arrhenius equation agreed satisfactorily with the experimental viscosity. The rate of lipid oxidation for unpurified salmon oil was temperature dependent ($R^2 = 0.99$). The activation energy for lipid oxidation of the oil was 51.3 kJ/mol. This study demonstrated that the Arrhenius equation could be used to evaluate the lipid oxidation rate and to predict the apparent viscosity of unpurified salmon oil.

In chapter two, the purification of salmon oil using adsorption, neutralization, and a combined neutralization and adsorption process were studied. Activated earth had a great ability as an adsorbent to adsorb PV, minerals, moistures, and insoluble impurities of the unpurified salmon oil. Neutralization significantly reduced FFA in the unpurified salmon oil but it increased PV. The combined method significantly reduced both PV and FFA in the salmon oils. All three purification processes had no severe effects on tocopherols.

The research for this Master of Science thesis shows that it is possible to produce purified salmon oil for human consumption from salmon processing wastes. The research findings will benefit the whole salmon industry and provide a good model for purification of oil from fish processing byproducts.

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